

Enhancement in corrosion resistance and electrical conductivity of hydrophobic-treated CP by PTFE emulsion containing TiN NPs

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Titanium nitride (TiN)-modified hydrophobic-treated carbon paper (CP) was prepared by impregnating CP with polytetrafluoroethylene (PTFE) emulsion containing TiN nanoparticles (NPs). Electrochemical measurements showed that CP witnessed an increase in corrosion resistance and electrical resistivity after treated with 5 wt% PTFE emulsion. Since the sacrifice in electrical conductivity is not beneficial to the application in proton exchange membrane fuel cells (PEMFCs), conductive ceramic NPs – TiN NPs were introduced into the CP to further improve its electrical conductivity. It was found that after adding TiN NPs, the electrical resistivity of CP (immersed in 5 wt% PTFE emulsion containing 8 wt% TiN NPs) decreased to a level (3.8 mΩ cm) similar to that of untreated CP (3.5 mΩ cm), and meanwhile there is a further improvement in corrosion resistance, where the corrosion current density (at 1.4 V) of TiN-modified CP stabilises at the lowest value of 5.50 μA/cm², as compared with 32.8 and 12.7 μA/cm² for raw CP and PTFE-treated CP. According to microstructure characterisation, these improvements could be attributable to the formation of conductive networks and improved PTFE distribution due to the addition of TiN NPs.

1. Introduction: Increasing consumption of fossil fuel in recent years has triggered the development of hydrogen energy industries [1], among which the proton exchange membrane fuel cells (PEMFCs) have become one of the hot topics. As the key component of the membrane electrode assembly of PEMFC, gas diffusion layer (GDL) has been extensively investigated to improve the performances of PEMFC [2]. Since it mainly serves as gas distributor and water drainage media that are closely related to cell performance, a good balance between porosity, permeability, hydrophobicity, corrosion resistance and electrical conductivity is normally required [3, 4]. Typically, hydrophobic-treated CP by PTFE impregnation is widely applied as GDL substrate. One of its degradation mechanisms [5] during operation is the dissolution effect of electrolyte, which occurs more readily when there is an increasing interfacial potential result from hydrogen starvation situations during start-up of PEMFC. The dissolution of carbon can cause loss of hydrophobicity (e.g. PTFE coating exfoliation) and even structure breakdown, which is detrimental to the water management and hence adversely affect the fuel cell performances [6].

Accordingly, enhancing the corrosion resistance of CP without sacrificing electrical conductivity is of great importance in improving performances of GDL. Ha *et al.* [7] found that the PTFE regions in GDL are immune to the carbon corrosion, whereas the carbon components are more vulnerable to the attack of electrolyte. Improving the coverage of PTFE on CP is, therefore, an effective method to improve the corrosion resistance of GDL. Although this inference has been validated by Perry *et al.* [8], achieving this goal by solely increasing the PTFE concentration of impregnation solution is unsatisfactory because the electrical conductivity will be sacrificed due to the insulating nature of PTFE [9]. From the viewpoint of improving electrical conductivity, Okano *et al.* [10] summarised that carbon nanofibres (e.g. nanotubes, nanohorn, nanocoil etc.) with high aspect ratio are preferable for improving the electrical performance of GDL due to their good electrical conductivity and mechanical properties. Owejan *et al.* [11] introduced graphitised carbon materials into the GDL and found that there was a mitigation of carbon corrosion and better cell performances,

which were attributed to the better anti-corrosion performances and electrical conductivity of graphitised carbon.

On the basis of this, theoretically, adding corrosion resistant conducting agents into the GDL could achieve an improvement in both corrosion resistance as well as electrical conductivity. Owing to its excellent electrical conductivity and corrosion resistance [12], titanium nitride (TiN) can be employed as a conducting agent in PTFE coating to enhance the electrical conductivity and anti-corrosion performance of CP. An improvement in corrosion resistance of TiN-modified Ti bipolar plate has been reported by our previous work [13]. It could be inferred that introducing TiN nanoparticles (NPs) into the coating of CP could also increase the electrical conductivity and corrosion resistance of the CP, which will provide a new idea in preparing more durable and electrical-conducting GDL. In this work, three samples prepared under different impregnation conditions are investigated through a series of characterisations to clarify the feasibility of this idea.

2. Experimental procedures: TiN-PTFE-modified CP is prepared by an impregnation process as presented in Fig. 1. Homemade CP was prepared according to our previous publication [14], which sequentially involves the resin impregnation of non-woven carbon fabric, hot-pressing, carbonisation and graphitisation. After obtaining the CP, polytetrafluoroethylene (PTFE, 60 wt% Dupont) was diluted with deionised water to 5 wt%. Moreover, TiN-PTFE mixture was prepared by adding 8 wt% TiN NPs (99.9% TiN, Aladdin, China) into the diluted PTFE suspension before being ultrasonically treated for 2 h. The so-called hydrophobic treatment was achieved by dipping the raw CP into these mixtures for 40 s, and ultrasonic treatment was simultaneously applied to the dipping bath during the whole process. The as-received sample was then horizontally placed in a drying oven and kept at 80°C (air) for 1 h before experiencing a 1 h sintering process in the tube furnace (350°C, argon). The heat-treated sample (CP-TiN-PTFE) eventually experienced a natural cooling in the tube furnace before being investigated in terms of their electrochemical performances, electrical resistivity, microstructure, elemental distribution and hydrophobicity. To compare the

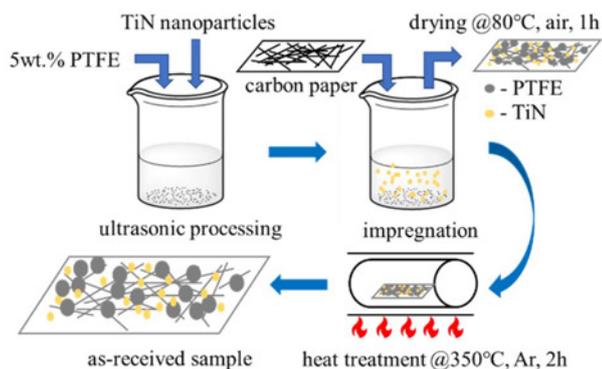


Fig. 1 Preparation procedure of the modified CPs

influences of TiN NPs, raw CP and PTFE-treated CP (CP-PTFE) (treated by 5 wt% PTFE solution under the same condition) were also characterised in this Letter.

In this Letter, the Tafel polarisation curve and electrochemical impedance spectroscopy (EIS) measurements were performed in the electrolyte of PEMFC (0.5 mol l⁻¹ sulphuric acid and 2 ppm hydrofluoric acid (HF)) through an electrochemical workstation (CHI660e, Shanghai Chenhua Instrument Co. Ltd. China), during which the CP was installed as a working electrode, while a saturated calomel electrode and a platinum sheet worked as reference electrode and counter electrode, respectively; the electrical resistivity of the samples were measured through a four-point probe (Series 2400 SourceMeter[®]). Note that the electrical resistivities were repeated for ten times at random places on CP (which was then averaged) to minimise the inaccuracies; the surface morphologies and elemental distribution were characterised by field-emission scanning electron microscope (JEOL.ISM-7600F) and transmission electron microscopy (TEM, JEM-2100F); moreover, the hydrophobicity (contact angle) was measured through sessile drop technique using Drop Meter A-100P optical contact angle meter (OCA20).

3. Results and discussion: The comparison of Tafel plot, potentiostatic polarisation and EIS result of the three samples are presented in Fig. 2, and the electrochemical parameters are tabulated in Table 1. It can be obtained from Fig. 2a that their corrosion potentials are 0.160, 0.191 and 0.184 V for CP, CP-PTFE and CP-8% TiN-PTFE, respectively, corresponding to corrosion current densities at 1.35, 0.13 and 0.05 $\mu\text{A}/\text{cm}^2$. This demonstrates that the presence of PTFE coating will increase the corrosion resistance of CP, and the addition of TiN NPs will further suppress the corrosion process. Additionally, the durability of the three samples is examined via 10 h potentiostatic polarisation studies at 1.4 V. As shown in Fig. 2b, owing to the wetting of carbon fibres and formation of passivation film, the current density experienced a quick decrease before stabilising at a specific value. Specifically, the current densities of CP, CP-PTFE and CP-TiN-PTFE reached a plateau at 32.8, 12.7 and 5.50 $\mu\text{A}/\text{cm}^2$, respectively. It can be noted that the presence of PTFE is capable of minimising the current densities of CP. Moreover, the CP immersed in PTFE solution containing TiN NPs exhibits the lowest current density, indicating a stable and better corrosion resistance as compared with rest of the samples.

The corrosion kinetic of the samples is further revealed by EIS, showing that all samples possess semi-circular arc with different radii, whose equivalent circuits and fitting parameters are summarised in Fig. 2c and Table 1. Owing to the absence of coating material, the EIS spectrum of raw CP shows a simple semi-arc, whose equivalent circuit can be understood as a single capacitor. R_s denotes protonic conduction resistance of electrolyte between electrodes, which can be obtained from Z' value at the high-frequency intercept. Q stands for constant phase element (CPE)

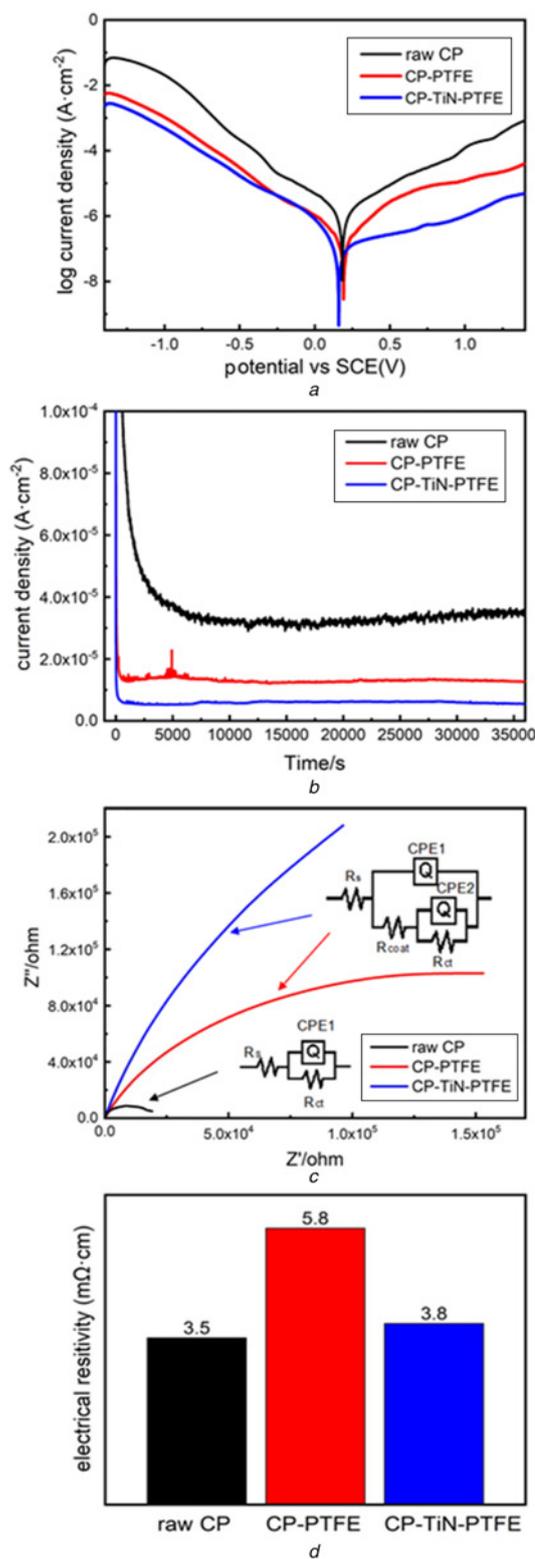


Fig. 2 Comparisons of
a Tafel curves
b Potentiostatic polarisation patterns
c Nyquist curves
d Electrical resistivity, between raw CP, CP-PTFE and CP-TiN-PTFE

originating from charge-transfer resistance during oxygen reduction. Moreover, R_{ct} is ascribed to the charge-transfer resistance at the interface of CP/electrolyte. By contrast, owing to the presence of the coating layer, the spectra of CP-PTFE and CP-TiN-PTFE display a circuit containing two capacitors. Therefore, another

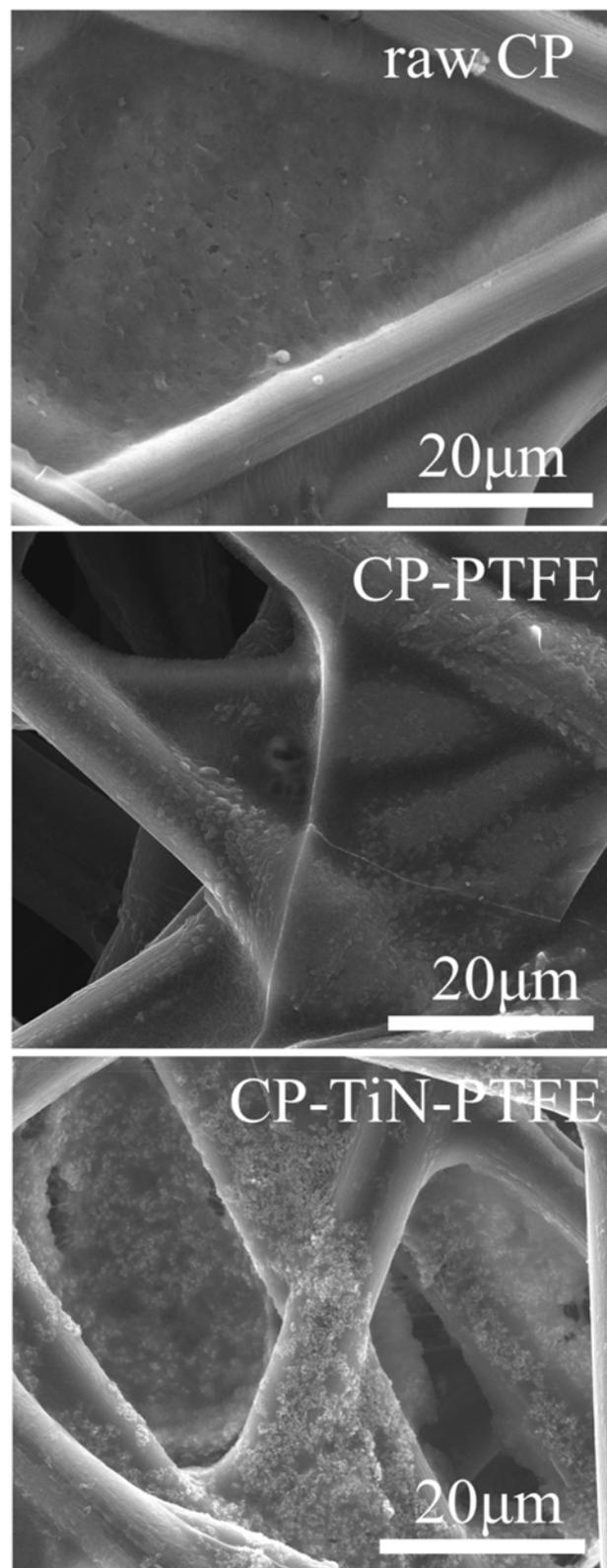
Table 1 Electrochemical parameters of different samples

	Raw CP	CP-PTFE	CP-TiN-PTFE
corrosion potential, V	0.184	0.191	0.160
corrosion current density, $\mu\text{A}/\text{cm}^2$	1.413	0.158	0.056
corrosion current density (at 1.4 V, $\mu\text{A}/\text{cm}^2$)	32.8	12.7	5.50
n_1	0.82	0.78	0.82
chi-squared	4.7×10^{-3}	4.10×10^{-3}	2.58×10^{-3}
R_s , $\Omega \text{ cm}^2$	3.03	2.90	2.37
CPE1	5.74×10^{-4}	2.85×10^{-5}	4.44×10^{-6}
R_{coat} , $\Omega \text{ cm}^2$	—	2.23×10^{-5}	9.97
n_2	—	0.85	0.86
CPE2	—	9.90×10^{-5}	3.62×10^{-5}
R_{ct} , $\Omega \text{ cm}^2$	2.68×10^{-4}	1.07×10^{-5}	1.18×10^{-6}

CPE and R_{coat} (representing the resistivity of coating material) are involved to fit their EIS spectra. It is particularly notable that the R_{ct} value increases from 2.68×10^4 to $1.07 \times 10^5 \Omega \text{ cm}^2$ with the introduction of PTFE, which enhanced further to $1.18 \times 10^6 \Omega \text{ cm}^2$ after adding TiN NPs. Since higher R_{ct} value generally symbolises better anti-corrosion capability [13], it can be concluded that adding TiN in PTFE coating can improve the anti-corrosion property of PTFE-treated CP. Besides, the R_{coat} value was observed to decline from 2.23×10^5 to $9.97 \Omega \text{ cm}^2$ after adding TiN, which manifests that the electrical conductivity of PTFE-treated CP was improved by adding TiN. Such an inference can also be verified by comparing their electrical resistivity measured by the four-point probe (Fig. 2d), where the electrical resistivity is 3.5, 5.8 and $3.8 \text{ m}\Omega \text{ cm}$ for raw CP, CP-PTFE and CP-TiN-PTFE, respectively. The improved electrical conductivity can be explained by the formation of conductive networking of TiN, which provides more pathways for electron motion.

Fig. 3 presents the surface morphologies of the three samples. All CPs display randomly entangled carbon fibres being connected by carbonised phenolic resin (pyrolytic carbon). After impregnated with PTFE, numerous PTFE islands are observable on CP-PTFE, which are formed due to the fusion of PTFE particles during heat treatment. They tend to reside on the pyrolytic carbon of raw CP and can be rarely observed on the carbon fibres. By contrast, the surface of CP-TiN-PTFE is further roughened with PTFE-TiN composite coating. Instead of being confined on pyrolytic carbon, coating material tends to sprawl along the carbon fibres and exhibit better surface coverage. Furthermore, the line scanning patterns of cross-sections of CP-PTFE and CP-TiN-PTFE are presented in Figs. 4a and b. Notably, the through-plane fluorine distribution became more intense and uniform as the presence of TiN NPs. The fluorine atoms in CP-PTFE prefer to congregate at only a few regions across the CP, which might be related to the flow of PTFE particles during the air-drying process. In contrast, for CP-TiN-PTFE, the signal originating from TiN is weak but stable, indicating that there is no apparent segregation of TiN. Besides, the signal of fluorine can be detected at both sides of CPs as well as the middle part of cross-section, which signifies that adding TiN NPs can improve the distribution of PTFE in CPs. A similar conclusion can be drawn based on Figs. 4c and d, where the fluorine atoms on CP-PTFE tend to segregate at the corner of carbon fibre junctions or pyrolytic carbon, while the fluorine distribution of CP-TiN-PTFE is more homogeneous on CP-TiN-PTFE. This validates again that the distribution of PTFE on CP can be improved by adding TiN NPs into impregnation solution.

The improved distribution of PTFE could be interpreted by the aggregation of TiN NPs in the CP. Owing to the high surface to volume ratio of nanosized particles, so-called homoaggregation

**Fig. 3** Surface morphology of samples in this Letter

and heteroaggregation will occur [15] when the CP was impregnated with an emulsion containing microsized (PTFE) and nanosized (TiN) particles. The TiN NPs tend to attach on the carbon fibre, aggregate with each other or with PTFE particles. The compact cluster of the aggregated particles gradually becomes a continuous TiN-PTFE composite on the CP, forming a tight and continuous coating after sintering. By contrast, for the impregnation

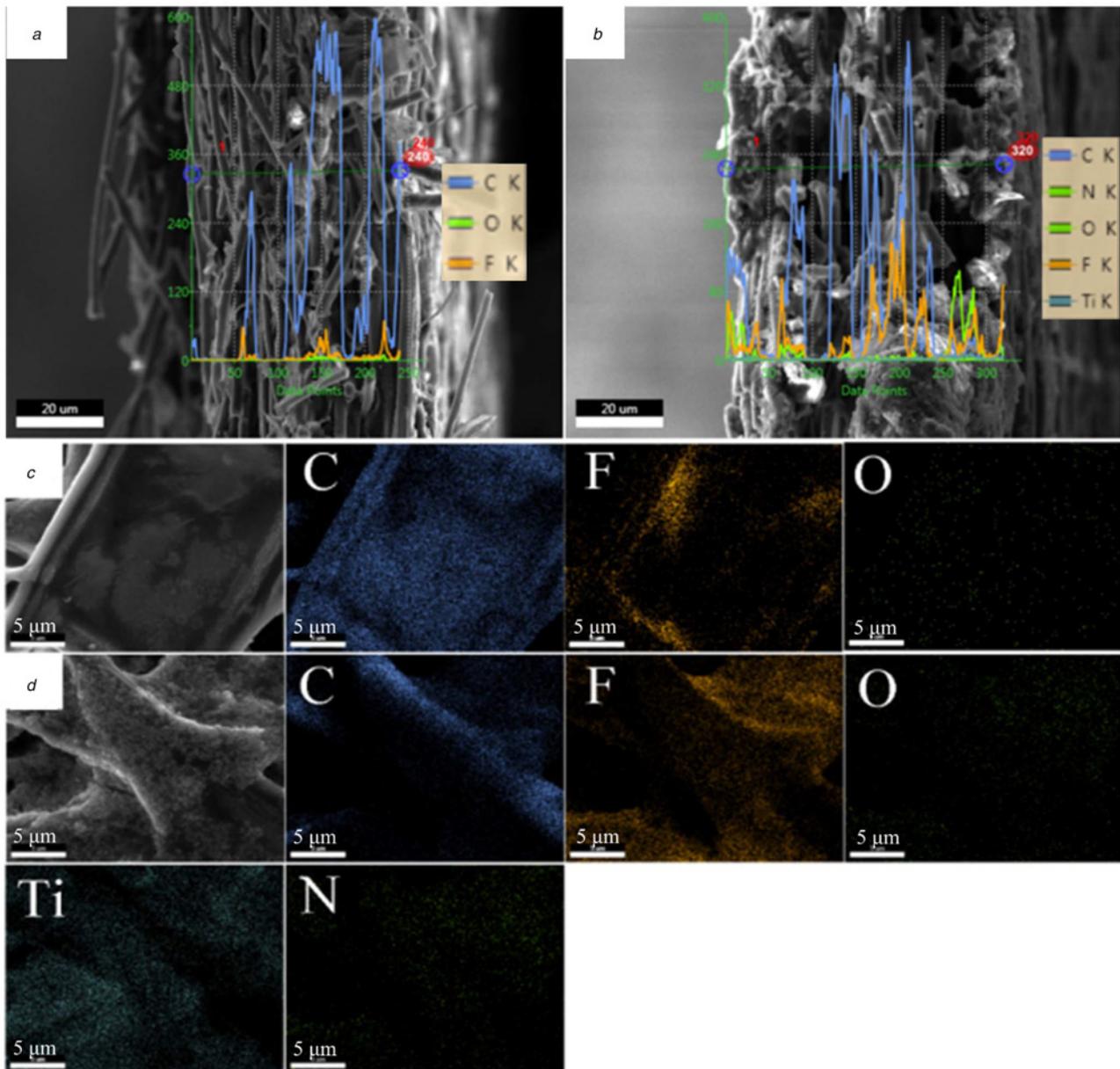


Fig. 4 Line scanning patterns of cross-sections of CP-PTFE and CP-TiN-PTFE
a, b Cross-sectional elemental distribution of CP-PTFE and CP-TiN-PTFE
c, d Energy-dispersive X-ray spectroscopy mapping of CP-PTFE and CP-TiN-PTFE

with unmodified PTFE solution, such a process is weak and negligible, which means the majority of particles tend to distribute at the trapping sites (e.g. fibre clusters and pyrolytic carbon) rather than spread along the fibres (Fig. 3).

Fig. 5 compares the variation in contact angle and surface morphology of CP-PTFE and CP-TiN-PTFE after 10 h of potentiostatic polarisation test at 1.4 V. Owing to the improved distribution of PTFE, CP-TiN-PTFE displays a slightly higher contact angle ($\sim 137^\circ$) than that of CP-PTFE (132°). Such an improvement indicates the enhanced efficiency of hydrophobic treatment by incorporating TiN NPs into the impregnation solution. After the accelerated corrosion test, the contact angles of both samples experience a downward trend to $\sim 106^\circ$ and $\sim 123^\circ$ for CP-PTFE and CP-TiN-PTFE, respectively. This decrease can be ascribed to the exfoliation of PTFE coating as well as the introduction of oxygen-containing groups during the corrosion [14]. Since TiN-modified CP has better corrosion resistance caused by the improved coating coverage, its variation in contact angle is

smaller than that of CP-PTFE, signifying an alleviation in hydrophobicity loss during corrosion. The good retention of hydrophobicity is another indicator of improved durability of CP, which means a stable water-management performance during the operation of PEMFCs [16].

A further observation by TEM (Fig. 6) reveals that there is a good bonding between PTFE and TiN in CP-TiN-PTFE, where the region with a lattice spacing of 0.21 nm should be TiN NPs, and the regions with a spacing of 0.35 nm can be regarded as uncoated carbon fibre. Besides, a semi-continuous PTFE region can be observed between these two regions. This demonstrates that TiN NPs were successfully introduced into the PTFE coating on CP. Since TiN is capable of withstanding various corrosion attacks, its presence on the CP can offer much tougher protection as compared with PTFE coating, thus yielding better anti-corrosion performances of the TiN-modified CP. Simultaneously, owing to the improved PTFE coverage on the CP, the contact of CP with electrolyte is largely eliminated, which works synergistically with the

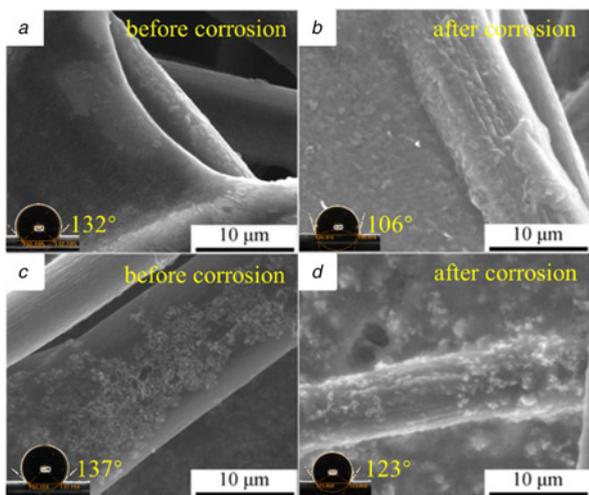


Fig. 5 Contact angle and surface morphology of
 a, b CP-PTFE
 c, d CP-TiN-PTFE before and after the accelerated corrosion test

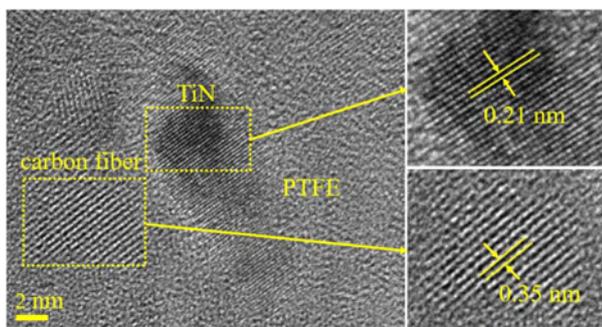


Fig. 6 TEM observation of CP-TiN-PTFE

previous factor, further endowing the CP with better corrosion resistance. Additionally, these NPs tend to embed in the PTFE coating, which can offer more routes for the flow of electrons in the CP, thus bringing better electrical conductivity and presumably better performances of PEMFCs.

4. Conclusion: TiN NPs were added into the PTFE emulsion used for the hydrophobic treatment of CP. Comparison between untreated CP, PTFE-treated CP and TiN-PTFE-treated CP shows that the addition of TiN NPs in impregnation solution can endow the treated CP with better corrosion resistance, whose corrosion current and corrosion potential are $0.056 \mu\text{A}/\text{cm}^2$ and 0.160 V , respectively. Besides, its corrosion current stabilises at $\sim 5.50 \mu\text{A}/\text{cm}^2$ during the 10 h potentiostatic test at 1.4 V , and its contact angle still maintains at 123° after the 10 h accelerated corrosion test. The improved corrosion resistance and durability of TiN-PTFE-treated CP can be ascribed to the improved PTFE distribution and the presence of TiN-PTFE composite coating. Last thing worth mentioning is that TiN NPs tend to introduce

conductive networking into PTFE coating, which can increase the electrical conductivity of PTFE-treated CP. This finding provides an efficient way to improve the corrosion resistance of hydrophobic-treated CP without sacrificing the electrical conductivity, which could be applied to produce more durable GDL, paving the way for the development of PEMFCs. The formula of impregnation solution could be further optimised to find the best combination of corrosion resistance and electrical conductivity of the impregnated CP.

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